employed for predicting the ternary data without including any ternary constants. The calculated ternary γ values agree well with the data of Narinskii and of Wilson.

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NOMENCLATURE

a, b = constants in the Redlich-Kwong equation of state
B, C = constants in the Redlich-Kister equation
f = fugacity, psia
k = interaction constant
P = pressure, psia
R = gas constant
T = absolute temperature, ° K
v = molal volume, cu ft/lb mole
x = liquid phase composition
y = vapor phase composition
γ = activity coefficient
ϕ = fugacity coefficient
Ω_a, Ω_b = parameters in the Redlich-Kwong equation of state

Subscripts

c = critical property
i, j = components of mixture
ij = interaction property
L = liquid phase
V = vapor phase
a, b = first and second components respectively

Superscripts

^{0} = reference state
$\bar{}$ = partial molar property
$\hat{}$ = solution property

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Vapor-Pressure Relationships for Hexafluorides

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Vapor pressure data for nine hexafluorides were fitted to the Frost-Kalkwarf equation, $\log P = A + B/T + C \log T + D(P/T^2)$. A reduced form of this equation was developed which requires the critical temperature, critical pressure, and Pitzer's ω factor for application. Sublimation pressure data for 13 hexafluorides were fitted to a two constant equation, $\log P' = A' + B'/T$.

Several investigators have recently compared different vapor pressure equations to test their reliability over wide ranges of temperature and pressure (*15, 20, 27*). The Frost-Kalkwarf equation (*8*) as modified by Reynes and Thodos (*23, 24*) was found to be the best equation over the pressure range from 10 torr to the critical pressure (*15*). They presented this equation in the following form:

$$\log P_R = \beta \left(\frac{1}{T_R} - 1\right) + \left(\frac{9}{5}\beta + \frac{8}{3}\right) \log T_R + 0.1832 \left(\frac{P_R}{T_R^2} - 1\right) \qquad (1)$$

which requires knowledge of the critical temperature, the critical pressure, and the constant β.

Since the Frost-Kalkwarf equation has been found to represent vapor pressure data very well, it was chosen for this study with the hexafluorides. The hexafluorides were selected as a group because of their molecular symmetry and their increasing industrial importance.

DATA FOR HEXAFLUORIDES

An extensive search of the literature was performed to locate vapor pressure data for the hexafluorides. Sublimation pressure data were also obtained. Primary data sources are shown in Table I as well as values of the critical properties and the triple points. The critical proper-

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Table I. Sources of Vapor Pressure Data and Properties of Hexafluorides

	Source of data		Triple pt.		Critical pt.	
Molecule	Vapor-liquid	Vapor-solid	T, °K	P, torr	T, °K	P, atm
SF_6	*(6, 16, 21, 26)*[a]	*(16, 17, 26)*	222.35[b] *(33)*		318.73	37.10 *(6)*
SeF_6		*(10, 33)*	238.45[b] *(28)*			
MoF_6	*(19, 25)*	*(25)*	290.55	398.1 *(3)*		
RuF_6		*(5)*				
RhF_6		*(4)*				
TeF_6	*(10)*	*(10, 33)*	235.35[b] *(33)*			
XeF_6		*(31)*	319.15[b] *(31)*			
WF_6	*(2, 25)*	*(25)*	275.15	413.2 *(3)*	451.35	46.3 *(1)*
ReF_6	*(12, 13)*	*(12, 13)*	291.85	436.5 *(3)*		
OsF_6	*(3)*[c]	*(3)*[c]	306.55	474.5 *(3)*		
IrF_6	*(3)*[c]	*(3)*[c]	316.95	518.8 *(3)*		
PtF_6	*(30)*	*(30)*	334.45	586 *(30)*		
UF_6	*(11, 18, 29)*	*(18, 29)*	337.15	1137.9 *(32)*	503.35	45.5 *(18)*
NpF_6	*(32)*	*(32)*	328.25	758.0 *(32)*		
PuF_6	*(7*[c]*, 32)*	*(7*[c]*, 32)*	324.74	533.0 *(32)*		

[a] Numbers in parenthesis refer to references. [b] Melting point. [c] Original data not reported.

ties have been measured for only three of the hexafluorides: sulfur, tungsten, and uranium.

Vapor pressure and sublimation pressure data are plotted in Figure 1 for 13 hexafluorides. Volatility is highest for sulfur hexafluoride and lowest for xenon hexafluoride.

DEVELOPMENT OF EQUATIONS

In their original development, Frost and Kalkwarf presented the following vapor pressure relationship (*8*):

$$\log P = A + B/T + C \log T + D\, P/T^2 \qquad (2)$$

where P is the vapor pressure in torr and T is the temperature in °K. Since the last term in this equation accounts for curvature between the boiling point and the critical point, it has been included only for the three hexafluorides for which data are available in this region. The constants in Equation 2 have been evaluated by a least-squares method using a Burroughs B5500 computer. Constants for nine hexafluorides and the standard error are shown in Table II. Since constants are available for rhenium, platinum, and neptunium hexafluorides in the original publications, these values are reported in the table.

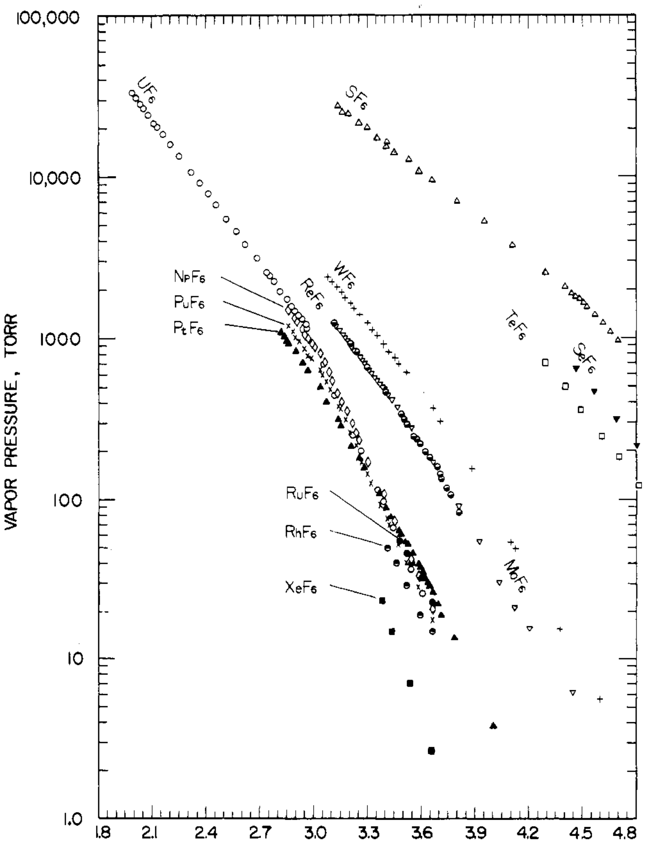

Figure 1. Vapor and sublimation pressure data for the hexafluorides

The Frost-Kalkwarf equation in reduced variables of temperature ($T_R = T/T_C$) and pressure ($P_R = P/P_c$) was first reported by Hamrin and Thodos (*9*) in the following form:

$$\log P_R = \alpha + \beta/T_R + \gamma \log T_R + \delta\, P_R/T_R^2 \qquad (3)$$

where $\delta = 0.1832$, and the boundary condition at the critical point is

$$\alpha + \beta + 0.1832 = 0 \qquad (4)$$

Comparison of Equations 2 and 3 shows that $B = \beta T_c$ and $C = \gamma$. In this study the constants α, β, and γ have been evaluated for sulfur, tungsten, and uranium hexafluorides. Combining these values and those for the inert gases (argon, krypton, and xenon) yields the following linear relationship

$$\gamma = 1.97\, \beta + 3.17 \qquad (5)$$

established by least squares where:

$$r = \sum_{i}^{n} (\gamma_i - \overline{\gamma})(\beta_i - \overline{\beta}) \Big/ \left[\sum_{i}^{n} (\gamma_i - \overline{\gamma})^2 \sum_{i}^{n} (\beta_i - \overline{\beta})^2\right]^{1/2} = 0.997$$

Equation 5 is in good agreement with the general relationship developed by Reynes and Thodos (*24*) for 30 polar and nonpolar substances:

$$\gamma = 1.8\, \beta + 2.67 \qquad (6)$$

The critical temperatures of the hexafluorides can be predicted from Equation 5 rewritten in terms of B and C as follows:

$$T_c = B/(0.508C - 1.61) \qquad (7)$$

Using the constants in Table II, one obtains the results shown in the last column of this table. The calculated critical temperatures show a 0.2% deviation for SF_6, 2.2% for WF_6, and 2.9% for UF_6.

Reduced Vapor Pressure Equation and Pitzer's Acentric Factor. Substitution of Equations 4 and 5 into Equation 3 results in an equation similar to Equation 1 with β as the only constant,

Table II. Constants for Vapor Pressure Equation and Calculated Values for Hexafluorides

Molecule	A	B	C	D	ω	Std error, %[a]	Calcd T_c, °K
SF_6	23.4158	−1453.18	−5.8278	0.6598	0.216	1.131	318
MoF_6	19.5362	−2019.68	−4.0518	0	0.097	0.182	551
TeF_6	18.3474	−1387.30	−4.0306	0	0.096	1.107	380
WF_6	27.6018	−2252.80	−6.8905	1.0562	0.270	0.483	441
ReF_6 *(12)*	18.2081	−1956.70	−3.5990	0	0.067	0.097	570
PtF_6 *(30)*	89.1496	−5685.8	−27.485	0		0.097	366
UF_6	25.4440	−2419.05	−6.0275	1.3389	0.247	4.927	518
NpF_6 *(14)*	14.6125	−1913	−2.3470	0	−0.015	0.124	683
PuF_6	12.1525	−1808.01	−1.5362	0	−0.068	0.085	757

[a] Standard Error = $\left[\sum_{1}^{n}\left(\frac{\text{Exptl} - \text{Calcd}}{\text{Exptl}}\right)/n\right]^{1/2}$.

$$\log P_R = \beta\left(\frac{1}{T_R} - 1\right) + (1.97\,\beta + 3.17)\log T_R + 0.1832\left(\frac{P_R}{T_R^2} - 1\right) \tag{8}$$

Since β is a constant limited to reduced vapor pressure correlations, it seemed desirable to relate it to a more widely accepted and tabulated quantity. Pitzer's acentric factor, ω, was chosen, which is defined as

$$\omega = -\log P_R - 1.00 \tag{9}$$

at $T_R = 0.7$ *(22)*. This definition in combination with Equation 8 yields

$$\beta = -2.64 - 8.10\,\omega - 0.30 \times 10^{-\omega} \tag{10}$$

To facilitate conversion between ω and β values, this relationship is plotted in Figure 2. Pitzer's acentric factor was found for each hexafluoride using this plot and the values of β calculated from B and T_c shown in Table II. When available, experimental T_c values were used.

Finally, Equation 10 can be substituted into Equation 8 to produce the reduced Frost-Kalkwarf equation in terms of ω,

$$\log P_R = (2.46 + 8.10\,\omega + 0.30 \times 10^{-\omega}) - (2.64 + 8.10\,\omega + 0.30 \times 10^{-\omega})(1/T_R) - (2.03 + 15.96\,\omega + 0.59 \times 10^{-\omega}) \times \log T_R + 0.18\,(P_R/T_R^2) \tag{11}$$

Computer solution has been carried out for ω values ranging from 0 to 0.4; the results are shown in Figure 3. For $\omega = 0$ the line shown coincides with Pitzer's original tabulation of reduced vapor pressure *(22)*. Although Equation 11 and Figure 3 were developed from inert gas and hexafluoride vapor pressure data, they should also be applicable to other substances for which T_c, P_c, and ω values are known. Figure 4 permits comparison of Equation 11 with the vapor pressure data of sulfur hexafluoride ($\omega = 0.216$), tungsten hexafluoride ($\omega = 0.270$), and uranium hexafluoride ($\omega = 0.247$). The solid lines represent Equation 11 for ω values of 0.216 and 0.270. Agreement is shown to be excellent.

Sublimation Pressure. Several of the hexafluorides exhibit a sublimation pressure greater than 1 atmosphere below their triple points as shown in Figure 1. Data for the sublimation pressure were available for 13 hexafluorides. They were fitted to a two-constant equation

$$\log P' = A' + B'/T \tag{12}$$

by a least-squares procedure. Values of the constants and an average heat of sublimation are tabulated in Table III.

Those hexafluorides for which T_c was available (calculated or experimental) were used to determine constants for a reduced form of Equation 12.

$$\log P_R' = \alpha' - \beta'/T_R \tag{13}$$

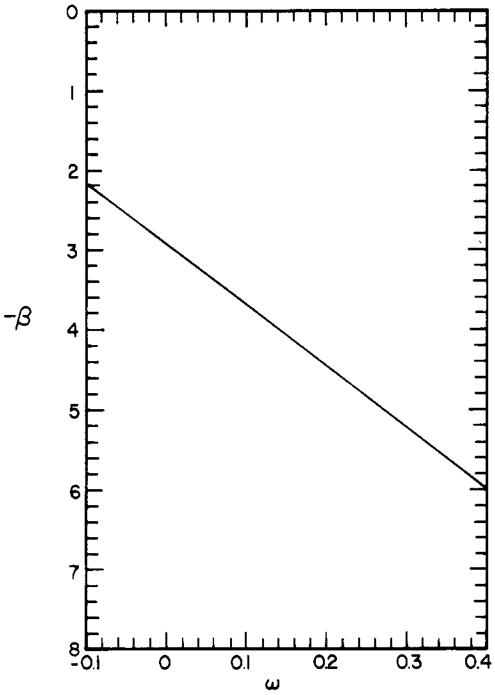

Figure 2. Relationship between reduced Frost-Kalkwarf equation constant, β, and Pitzer's acentric factor ω

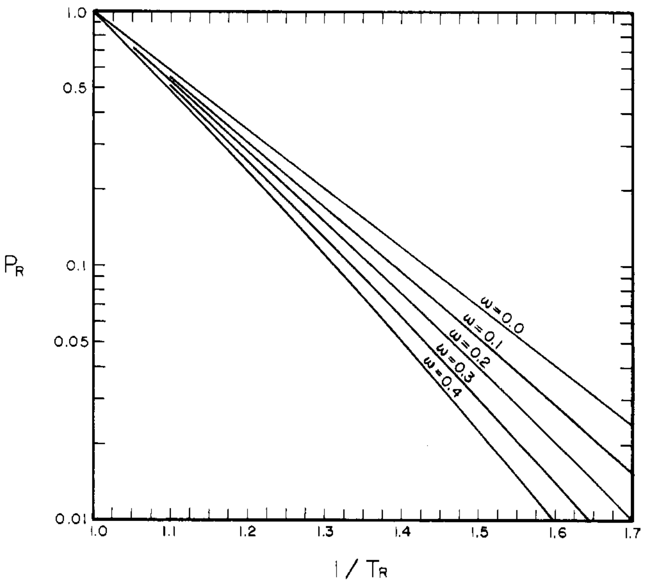

Figure 3. Reduced vapor pressure correlation (Equation 11) with ω as parameter

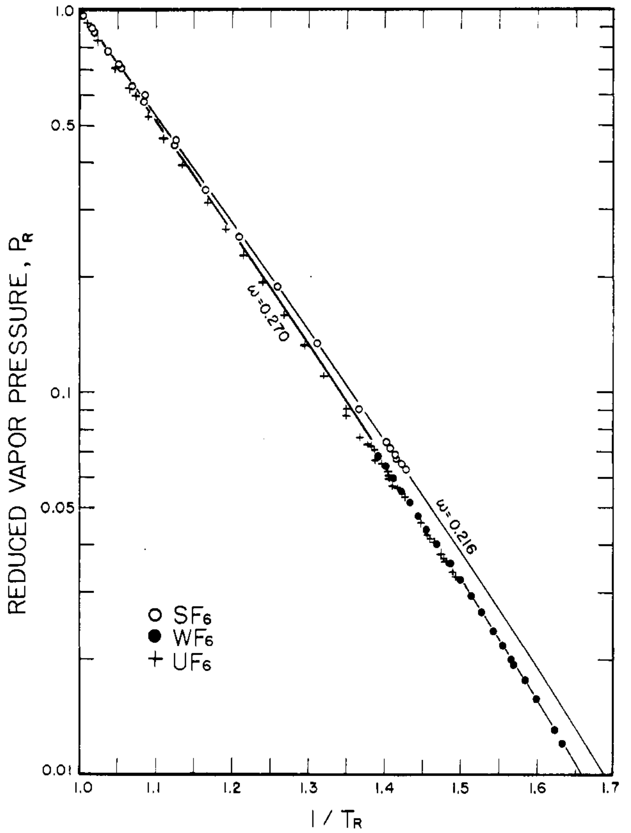

Figure 4. Log P_R vs $1/T_R$ for sulfur, tungsten, and uranium hexafluoride

Table III. Constants for Sublimation Pressure Equation and Average Heat of Sublimation for Hexafluorides

Molecule	A'	$-B'$	ΔH^a, kcal/g mole
SF_6	8.79	1236	5.65
SeF_6	9.16	1423	6.51
MoF_6	9.02	1861	8.51
RuF_6	8.95	2071	9.48
RhF_6	9.01	2144	9.81
TeF_6	9.56	1561	7.14
XeF_6	12.63	3332	15.2
WF_6	9.81	1973	9.03
ReF_6	8.60	1742	7.97
PtF_6	9.10	2102	9.62
UF_6	10.80	2608	11.9
NpF_6	10.63	2543	11.6
PuF_6	10.56	2545	11.6

[a] These are average values based on solid phase data neglecting solid phase transitions. Cady and Hargreaves (*3*) found such transitions for MoF_6, WF_6, and ReF_6. A transition is also reported for PtF_6 (*30*).

Values of α' ranged from $3.75 \leqq \alpha' \leqq 6.26$ and β' from $3.06 \leqq \beta' \leqq 5.75$. Average values give the following relationship for the sublimation pressure of the hexafluorides

$$\log P'_R = 5.09 - 4.07/T_R \qquad (14)$$

It is recommended that Equation 12 be used with the constants in Table III to calculate sublimation pressures. When critical properties of more hexafluorides are measured, the validity of a reduced equation for the solids can be determined.

NOMENCLATURE

A, B, C, D = constants for Equation 2
A', B' = constants for Equation 12
P = vapor pressure, torr
P' = sublimation pressure, torr
P_c = critical pressure, torr
P_R = reduced vapor pressure, P/P_c
P'_R = reduced sublimation pressure, P'/P_c
T = absolute temperature, °K
T_c = critical temperature, °K
T_R = reduced temperature, T/T_c

Greek Letters

$\alpha, \beta, \gamma, \delta$ = constants for Equation 3
α', β' = constants for Equation 13
ω = acentric factor

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